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Phosphorus-Nitrogen Synergism in Fire Retarding Styrenic Polymers: Some Preliminary Studies

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Introduction

The primary strategies to improve the fire retardance of commercially important styrene-based polymers are largely reliant on halogenated fire retardants (FRs). Currently, these compounds are considered to be hazardous to public health and environment. As a result, many halogen-based FRs have been withdrawn, especially, from their use in products that form construction elements in built environments [1]. Thus, it is necessary to develop efficient fire-retardant systems for mitigating their hazardous impact in fire scenarios. Among the proposed FR solutions, the compounds containing P atoms can be very powerful in inhibiting the ignition, and often supress the combustion of polymeric materials effectively [2].

Here, we report preliminary results on the chemical incorporation of various P- and/or N- containing unsaturated compounds into polystyrene (PS) via *co-* and *ter-* polymerisations and characterisations of the modified materials with regards to their thermal degradation and combustion attributes. The primary aim of this study to find the effective combination of P- and N- containing compounds that can trigger P-N synergism, thus enhancing fire retardance of PS. The compounds such as diethyl(acryloyloxymethyl)phosphonate (DEAMP), diethyl-*p*-vinylbenzyl phosphonate (DEpVBP), acrylic acid-2-(diethoxyphosphorylamino)ethyl ester (ADEMPAE), maleimide (MI), acrylamide (AM) and N,N-dimethyl acrylamide (DMA) had been used for the modification of PS. The fire performance of unmodified PS and modified PS was determined using a range of standard techniques. They included bomb calorimetry, thermo-gravimetric analysis (TGA), differential scanning calorimetry (DSC), Fourier Transform Infrared (FT-IR) spectroscopy, Nuclear Magnetic Spectroscopy (NMR).

Materials

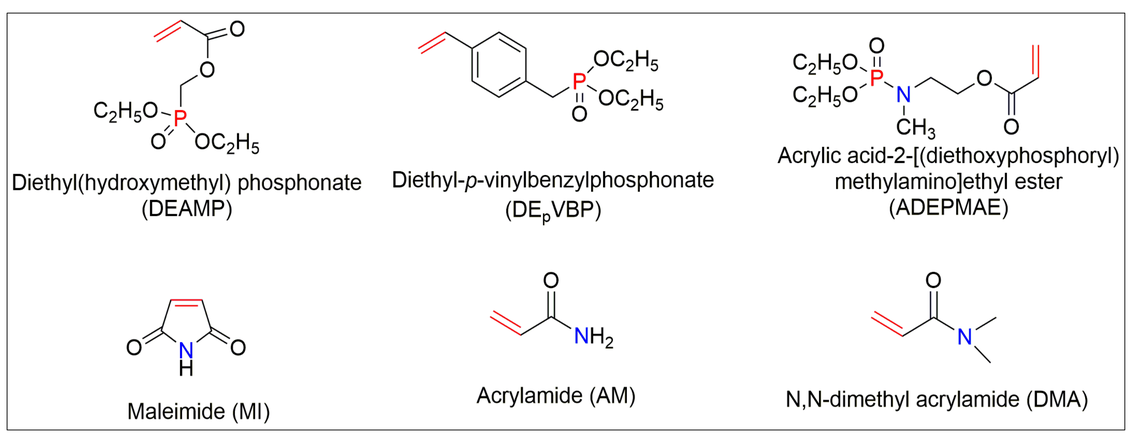

Figure 1: Chemical structures of P-,P/N- and N-containing compounds

Procedure

- *Co-* and *ter*-polymers of styrene (St) were primarily prepared through free-radical polymerisation reactions in toluene/DMF using 2,2'-azobisisobutyronitrile (AIBN) as the initiator, at 60 °C for about 6-16 hours, under an atmosphere of argon.
- The polymeric products, were recovered by precipitation into an excess of methanol, followed by drying to constant weight in a vacuum oven kept at *ca.* 50°C.

Methods

- Bomb calorimetry: Parr 6200 oxygen bomb calorimeter; gross calorific value measurements as per BS EN ISO 18125:2017
- TGA: Perkin Elmer Pyris 1 TGA instrument, *ca.* 8-9 mg samples, 30-800 °C temperature range, nitrogen and air atmospheres, at 10 °C/min heating rate.
- DSC: Mettler Toledo DSC 1 system, *ca.* 8-9 mg samples, 25 -600 ℃ temperature range, nitrogen atmosphere, at 50ml/min flow and 10 ℃/min heating rate.
- Fourier-Transform Infrared (FT-IR) spectra recorded in Attenuated Total Reflectance (ATR) mode on a Thermo Nicolet, Nexus spectrometer

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Results

The level of incorporation of monomers (P- and N-) kept as low as possible. The mole fraction of St/monomer in the feed was 0.90/0.10 mol/mol for *co*-polymers and 0.80/0.10/0.10 for *ter*-polymers. From the flammability and combustion studies of *co*-polymers, it is evident that all *co*-polymers of styrene increase the fire efficiency of PS (Table 1). However, it is more evident that styrenic *co*-polymers with DEAMP, DEpVBP, and MI were more efficient in enhancing fire retardancy of PS. It is clear from the decrease in the values of ΔH_{pyro} and ΔH_{comb} and increase in the char residue (TGA) of *co*-polymers such as St-DEAMP, St-DEpVBP and St-MI (Table 1 and figure 2). Therefore, from the list of FRs used for *co*-polymerisation of styrene, the most effective FRs groups such as DEAMP, DEpVBP and MI were used for preparing *ter*-polymers. The results proved that there is significant drop in ΔH_{pyro} and ΔH_{comb} of *ter*-polymers compared to that of *co*-polymers. For instance, ΔH_{comb} had reduced by 22.8% and 19.5% for the *ter*-polymers, St-DEAMP-MI and St-DEpVBP-MI respectively.

Table1: Heat of pyrolysis, heat of combustion and char residue of polymers measured in TGA in nitrogen and air atmosphere

Sample	ΔH_{pyro} (J/g)	ΔH_{comb} (J/g)	Residue in N_2 at 500°C (wt %)	Residue in N_2 at 800°C (wt %)	Residue in air at 500°C (wt %)	Residue in air at 800°C (wt %)
PS	717.0	40412	0.6	0.5	0.6	0.1
St-DEAMP	392.9	35453	7.8	6.2	22.3	2.2
St-DEpVBP	673.8	39268	5.4	4.0	17.8	1.9
St-ADEPMAE	701.0	38026	2.7	2.0	8.7	1.4
St-MI	659.6	34059	2.1	1.3	5.5	0.4
St-AM	663.0	39051	0.2	0.2	2.6	0.6
St-DMA	702.7	39963	0.4	0.2	2.6	0.4
St-DEAMP-MI	190.5	31267	25.2	22.2	44.6	3.1
St-DEpVBP-MI	162.3	32520	25.1	21.6	36.1	1.2

ΔH_{pyro} – heat of pyrolysis, ΔH_{comb} – heat of combustion

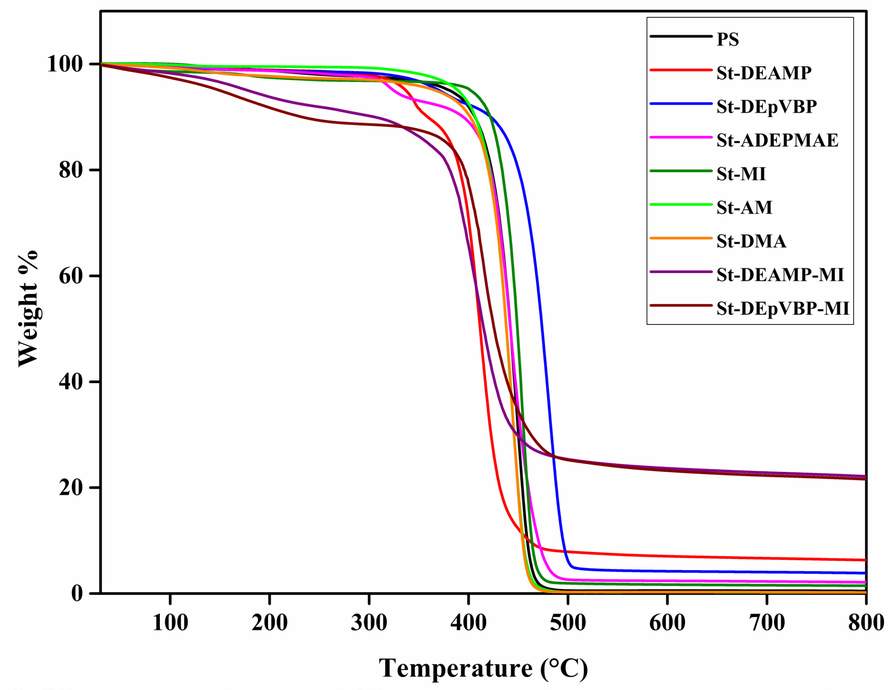

Figure 2: TG curves obtained at 10 ℃/min for styrenic polymers in nitrogen atmosphere

Conclusions

- The reactive modification of PS with P-, P/N- and N- containing monomers is found to be effective on improving the fire retardancy of PS.
- The general degradation profiles of *co*-and *ter*-polymers were found to be different from that of the unmodified PS, particularly, in terms of the degradation temperature, slopes and the amounts of char residues produced.
- Among various *co*-polymers, St-DEAMP, St-DEpVBP and St-MI exhibited better fire retarding performance compared to PS.
- The significant improvement observed for *ter*-polymers proved that P-N synergism can enhance the fire retardance of PS.
- As it is known that P-N synergism promotes charring during the combustion process, it is more pronounced in *ter*-polymers containing different P- and N- groups (an increase of nearly 90 %), than that of polymer (St-ADEPMAE) containing direct P-N bond.
- The exact fire retarding mechanism of these *ter*-polymers is not proposed at present, which is under study.

References

1. Morgan A.B.: The Future of Flame Retardant Polymers-Unmet Needs and Likely New Approaches. Polymer Reviews, **59**, 25–54 (2018).
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